Benzo[*b*]selenophen-2(3*H*)-one: Synthesis and Properties

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Benzo[*b*]selenophen-2(3*H*)-one has been prepared and characterized. It undergoes selenolactone ring opening reactions, reactions at the CH_2 group, and electrophilic substitution.

In contrast to its 3-oxo-isomer,[1,2] benzo[*b*]selenophen-2(3*H*)-one (I) has not been described hitherto. Many synthetic approaches have been studied without success, *viz.* (*a*) intramolecular electrophilic cyclisation of *Se*-phenyl chloroselenoacetate by analogy with a synthesis of benzo[*b*]selenophenquinone;[2,3] (*b*) oxidation, according to Dickinson's method for the sulphur series,[4] of the cyclotriboroxane obtained, in very low yield, from n-butyl borate and 2-lithiobenzo[*b*]selenophen; (*c*) cyclisation of 2-(benzylseleno)phenylacetonitrile to 2-aminobenzo[*b*]selenophen according to the method of Stacy [5] for sulphur compounds; and (*d*) synthesis of the diselenide (Va) from the diazotate derivative of the opened form of indolin-2-one and sodium diselenide.[6] The successful method, as for another lactonic isomer, selenophthalide,[7] involved cyclodehydration of the corresponding acid (IIIa).

The selenolactone (I) was in fact prepared in one step by the reaction of phosphinic acid in refluxing acetic acid or ethanol on the dequaternisation product of the selenonium salt resulting from the reaction of bromine on 2-methylselenophenylacetic acid (IIa).[8] Phosphinic acid, a useful reagent in organoselenium chemistry [9,10] reduces the selenium–bromine bond of the intermediate selenenyl bromide, prevents oxidation of the resulting selenol (IIIa), and facilitates its cyclodehydration. The selenolactone (I) can also be obtained similarly from the nitrile (IIb), but in lower yield.

This method of synthesis can be employed in the sulphur series. Chlorodemethylation of 2-(methylthio)-phenylacetic acid with sulphuryl chloride and treatment with phosphinic acid under the same conditions gives good yields of benzo[*b*]thiophen-2(3*H*)-one.[4,5]

To obtain the selenolactone (I), reducing conditions must be strictly maintained. Thus, after prolonged refluxing in ethanol, we obtained benzo[*b*]selenophen-2-ylphosphinic acid (XII) (see later).

The physicochemical characteristics of the lactone (I) agree with the proposed structure. The i.r. spectrum (CCl_4) showed a carbonyl vibration at 1 735 cm^{-1}, in the range expected for *Se*-phenyl selenoesters [11] (1 730 cm^{-1} for the corresponding thiolactone). The ^1H n.m.r. spectrum (CCl_4; internal standard hexamethyldisiloxane) revealed four aromatic (m, δ 7.00—7.20) and two benzylic protons (s, δ 3.83) (3.13 in benzene). In these solvents, no time-dependent prototropy was observed. The ^{13}C n.m.r. spectrum ($CDCl_3$; internal standard tetramethylsilane) showed a carbonyl signal at δ 204.9 (202.3 for the sulphur analogue; 174.1 for the oxygen analogue; 196.7 for *Se*-phenyl selenoacetate); a CH_2 resonance at 52.8 [47.1 (S); 33.0 (O)] [t, $J(^{13}C–H)$ 32 ± 3 Hz], the two quaternary carbon signals at 134.0 and 136.6, and four aromatic carbon resonances at 124.7, 126.2, 126.2, and 122.2. The decoupled ^{77}Se n.m.r.[12] spectrum showed a resonance at δ 584 (external standard dimethyl selenide) (the value for *Se*-phenyl selenoacetate is 660, and that for benzo[*b*]selenophen

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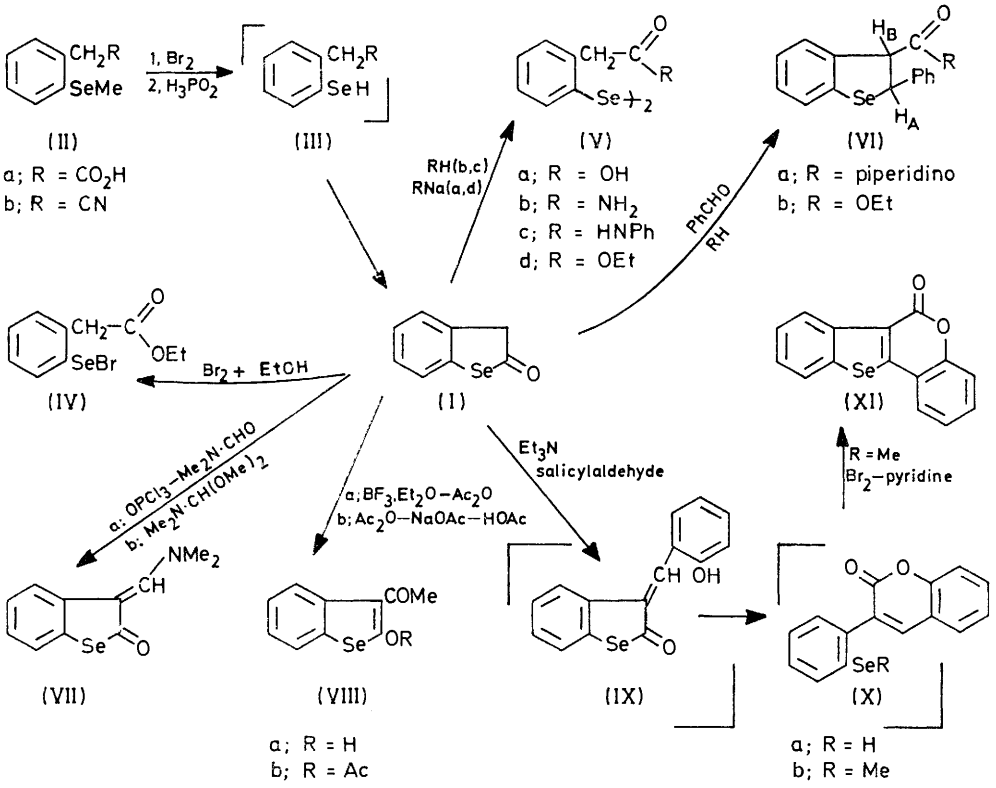
526). The mass spectrum confirms the presence of one selenium atom per molecule (correct isotopic ratio) and gives a molecular weight of 198 for ^{80}Se [$(C_8H_6OSe)^{+\cdot}$, 100%]. The following main fragments were noted: $(M - CO)^{+\cdot}$, *m/e* 170 (42.7%); $(M - CHO)^{+}$, 169 (64.3%); $(M - Se)^{+\cdot}$, 118 (28.6%); $(M - CO - Se)^{+\cdot}$, 90 (17.2%); $(M - CHO - Se)^{+}$, 89 (29%) [metastables for the transitions $(M)^{+\cdot} \longrightarrow (M - CO)^{+\cdot}$ and $(M)^{+\cdot} \longrightarrow (M - CHO)^{+}$].

The susceptibility to cleavage of the selenolactone ring of compound (I) makes it impossible to carry out electrophilic bromination and nitration (NO_2BF_4). These reactions lead to ring opening, giving the selenenyl halide (IV) and the diselenide (Va). Under the action of bases (NaOH, NH_3, $PhNH_2$, EtONa) the selenolactone (I) easily undergoes ring opening through conventional nucleophilic substitution leading to the diselenides (Va—d).

When the selenolactone (I) was submitted to the conditions of the Mannich reaction with benzaldehyde and piperidine, the amide (VIa), product of ring rearrangement, was isolated in high yield. Its structure was proved by n.m.r. spectroscopy (see Experimental section) and was supported by the low frequency carbonyl vibration at 1 620 cm^{-1} (KBr), as expected for a secondary amide, and indicating the loss of the selenolactone function. Treatment with benzaldehyde alone (in trimethylamine–ethanol) gives a corresponding rearrangement to the ester (VIb), which is similar to that recently shown to occur with the sulphur analogue of (I);[13] we consider that the reaction involves aldol condensation on the CH_2 group, ring opening of the selenolactone through nucleophilic attack by the secondary amine, and internal Michael addition by the SeH group. We believe that the aldol condensation precedes the ring opening. Indeed, compounds (V), which are of the same type as the expected product of preliminary ring opening, give no reaction with benzaldehyde under the same conditions.



SCHEME 1

Use of salicylaldehyde instead of benzaldehyde in triethylamine–ethanol gives a high yield of the selenium analogue (XI) of coumestan. Similar reactions have been reported recently in the sulphur series.[14,15] We consider that the preliminary aldol condensation product (IX) undergoes an internal transesterification to give the coumarin (Xa). This could undergo internal Michael addition on the double bond of the coumarin ring, followed by aromatisation. In the oxygen series[16] the reaction stops at the open intermediate corresponding to (Xa), and in the sulphur series at the dihydrothiocoumestan.[14,15] The elemental analysis (C,H) and mass spectrum of selenocoumestan (XI) agree with the proposed structure. In addition to the molecular ion

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[*m/e* 300 (100%) for ^{80}Se and isotope peaks for one atom of selenium per molecule], the following main fragments were found: $(M - CO)^{+\cdot}$, *m/e* 272 (22.5%); $(M - CO - CHO)^{+}$, 243 (13%); and $(M - CO - CHO - Se)^{+}$, 163 (15%) (metastable peaks were observed for each of these transitions). The carbonyl stretching frequency [1 720 cm^{-1} (KBr)] is consistent with the presence of a coumarin ring.

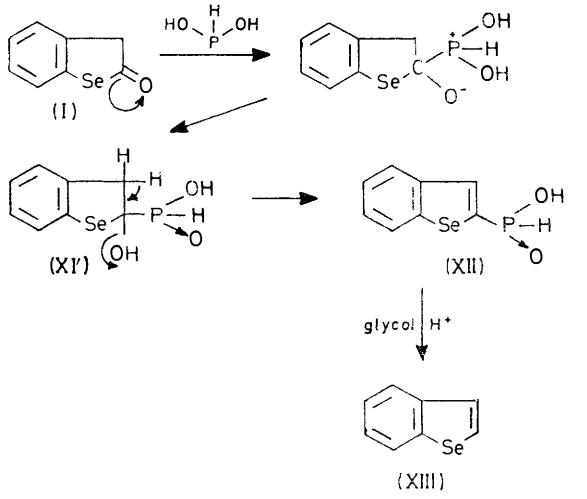
As a confirmation of the structure (XI) we carried out its unequivocal synthesis. Condensation of salicylaldehyde with the acid (IIa) provided the coumarin (Xb), which was cyclized by the bromine–pyridine method.[17]

A similar aldol condensation between the selenolactone (I) and dimethylformamide dimethyl acetal[18] gave compound (VII), identified by elemental (C, H, N) analysis and ^1H n.m.r., ^{13}C n.m.r., and mass spectra. The undecoupled ^{13}C n.m.r. spectrum exhibited the carbonyl signal ($CDCl_3$; Me_4Si) at δ 186.7, that of C-3 at δ 103.9 as a singlet [*cf.* 52.8 for the selenolactone (I)], indicating an ethylenic carbon atom, and another ethylenic carbon signal as a doublet at δ 115.8. The mass spectrum showed a molecular ion [*m/e* 253 (^{80}Se) (100%)], and demonstrated the presence of a single Se atom per molecule. The following fragments also appeared: *m/e* 210 [15.6%, $(C_9H_6OSe)^{+\cdot}$], 209 [51.7%, $(C_9H_5OSe)^{+}$], 182 [39.8%, $(C_8H_6Se^{+})$], 181 [24.6%, $(C_8H_5Se)^{+}$], 89 [10.1%, $(C_7H_5)^{+}$], and 63 [5%, $(C_5H_3)^{+}$] (metastable peaks for the transitions 209 ⟶ 181 and 210 ⟶ 182).

A similar reaction took place with the corresponding thiolactone.

The compound (VII) was also obtained as the only product of reaction of the selenolactone (I) under Vilsmeier–Haack conditions. A Friedel–Crafts reaction with acetic anhydride and boron trifluoride–ether led to acetylation at the 3-position; the product (VIIIa) was obtained as a complex with the catalyst, the formation of which probably prevents further *O*-acetylation. Compound (VIIIa) can be freed from the boron trifluoride complex by hydrolysis. It exists in the chelated hydroxy-form as shown by the very low field OH signal [δ 14.52 ($CDCl_3$)], which disappears on deuteriation, and the low value of the carbonyl frequency [1 610 cm^{-1} (KBr)]. The hydroxy-group of compound (VIIIa) is significantly more deshielded than in its isomer, 2-acetyl-3-hydroxybenzo[*b*]selenophen (δ 12.61).[19] A similar phenomenon has been observed in the corresponding 2,3-disubstituted thiophens.[20] The thio-analogue of (VIIIa), obtained in the same manner, shows a similar deshielding effect (δ_{OH} 14.51). Nucleophilic acetylation of compound (I) by acetic anhydride–acetic acid–sodium acetate gave the 3,*O*-diacetylated product (VIIIb). Similar treatment of the thio-analogue of (I) gives a 70 : 30 mixture of 3-acetyl and 3,*O*-diacetyl compounds. Compound (VIIIb) showed two carbonyl i.r. bands [1 650 and 1 770 cm^{-1} ($CHCl_3$)], and underwent quantitative hydrolysis to the 3-acetyl derivative (VIIIa).

The formation of benzo[*b*]selenophen-2-ylphosphinic acid (XII) after prolonged refluxing in ethanol of the reaction mixture for the preparation of the selenolactone (I) can be interpreted like the reaction of phosphinic acid on carbonyl compounds,[21] *i.e.* in terms of nucleophilic attack on the selenolactone carbonyl group by the phosphonous tautomeric form of phosphinic acid present in minor proportions[22] (Scheme 2), followed by dehydration of the resulting hydroxylated dihydrobenzo[*b*]selenophen (XI′). The phosphinic acid (XII) itself, treated with acid (HCl or H_3PO_2) in refluxing ethylene glycol, affords benzo[*b*]selenophen (XIII) through electrophilic protiodephosphination; this latter reaction is not observed in alcoholic media. Benzo[*b*]selenophen (XIII) can be obtained directly and quantitatively by treating the selenolactone (I) with phosphinic acid in refluxing ethylene glycol. In addition, the formation of benzo[*b*]selenophen has been detected when phosphinic acid and 2-(methylseleno)phenylacetic acid (IIa) are heated for a long time in ethylene glycol. Phosphinic acids similar to (XII) have also been isolated and shown to be reaction intermediates in the reduction by phosphinic acid of benzo[*b*]selenophen-3-ylphosphinic acid, of benzo[*b*]thiophen-3(2*H*)-one, and of selenochroman-4-one.[10]



SCHEME 2

We attribute to these phosphorus intermediates the phosphinic acid rather than the phosphonite ester tautomeric form (RO·PH·OH) since it is well known[23] that, on the one hand, this form is easily hydrolysed and, on the other, it exists only in the phosphinate form

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[$RO{\cdot}P(O)H_2$], which is excluded on the basis of n.m.r. spectroscopy (see Experimental section).

EXPERIMENTAL

The n.m.r. spectra were determined on the spectrometers of the University of Liège NMR Centre. Unless indicated to the contrary ^1H n.m.r. spectra were determined on a Varian T-60 instrument, with hexamethyldisiloxane as internal reference, and ^{13}C and ^{77}Se n.m.r. spectra on a Bruker HFX-90 spectrometer.

Benzo[b]*selenophen*-2(3H)-*one* (I).—To a stirred solution of 2-(methylseleno)phenylacetic acid (45.8 g, 0.2 mol) in the minimum quantity of chloroform, bromine (32 g, 0.2 mol) was added dropwise at room temperature. The precipitated selenonium salt was filtered off, dried (quantitative yield), resuspended in acetic acid (200 ml), and heated with stirring for 1 h at 80 °C. Aqueous 50% phosphinic acid (*ca.* 40 ml) was added dropwise until the colour disappeared. Concentrated hydrochloric acid (25 ml) was then added, and the mixture was refluxed for 4 h. After hydrolysis and the usual purification, the *lactone* (I) (29.5 g, 75%) was obtained as a white solid (from light petroleum), m.p. 75°. By a similar procedure compound (I) (25%) can be obtained from the nitrile (IIb) [8] (Found: C, 49.0; H, 3.1. C_8H_6OSe requires C, 48.75; H, 3.05%).

The sulphur analogue of (I) was also obtained (50%) in similar manner from 2-(methylthio)phenylacetic acid (0.2 mol), except that chlorodemethylation was effected by sulphuryl chloride (0.2 mol) for 3 h in chloroform.

Halogenation.—A solution of bromine (0.01 mol) in carbon tetrachloride (5 ml) was added dropwise at 0 °C to a solution of compound (I) (1.97 g, 0.01 mol) in carbon tetrachloride (30 ml). The mixture was set aside for 4 h, then evaporated under vacuum, and the residue was taken up in absolute ethanol (10 ml) for esterification. Next day the solvent was evaporated off. Crystallisation of the residue gave *ethyl* 2-(*bromoseleno*)*phenylacetate* (IV) (2.61 g, 80%), m.p. 48° (from light petroleum); $\nu_{C=O}$ (KBr) 1 675 cm^{-1}; δ ($CDCl_3$) 1.20 (t, Me, *J* 7 Hz), 3.75 (q, CH_2), 4.05 (s, CH_2), 7.00—7.30 (m, H-4, -5, and -6), and 7.70—8.00 (m, H-3) (Found: C, 37.7; H, 3.5. $C_{10}H_{11}BrO_2Se$ requires C, 37.25; H, 3.4%).

Opening of the Selenolactone Ring.—A solution of compound (I) (0.01 mol) in ethanol (25 ml) was heated under reflux with an excess of base (RH or RNa; see Scheme 1) (0.02 mol). The usual isolation gave the diselenides (V). *2,2′-Diselenobisphenylacetic acid* (Va) had m.p. 143° (92%) (from hexane–benzene); $\nu_{C=O}$ (KBr) 1 715 cm^{-1}; δ ($CDCl_3$) 3.65 (s, CH_2) and 7.00—7.20 and 7.54—7.65 (m, aromatic) (Found: C, 45.1; H, 3.3. $C_{16}H_{14}O_4Se_2$ requires C, 44.85; H, 3.25%). The *amide* (Vb) had m.p. 206° (73%) (from hexane–benzene); $\nu_{C=O}$ (KBr) 1 670 cm^{-1}; δ 3.54 (s, CH_2) and 7.00—7.20 and 7.45—7.80 (m, aromatic) (Found: C, 45.2; H, 3.9; N, 6.4. $C_{16}H_{16}N_2O_2Se_2$ requires C, 45.05; H, 3.75; N, 6.55%). The *anilide* (Vc) had m.p. 226° (60%) (from hexane–benzene); $\nu_{C=O}$ (KBr) 1 650 cm^{-1}; δ 2.55 (s, CH_2) and 7.00—7.90 (m, aromatic) (Found: C, 58.2; H, 4.2; N, 4.9. $C_{28}H_{24}N_2O_2Se_2$ requires C, 58.15; H, 4.2; N, 4.85%). The *ethyl ester* (Vd) had b.p. 215° at 3 mmHg (50%); $\nu_{C=O}$ (film) 1 770 cm^{-1}; δ 1.10 (t, Me, *J* 7 Hz), 2.60 (s, CH_2), 4.10 (q, CH_2), and 7.50—8.10 (m, aromatic) (Found: C, 49.55; H, 4.7. $C_{20}H_{22}O_4Se_2$ requires C, 49.6; H, 4.55%).

Mannich Reaction of the Lactone (I).—To a solution of compound (I) (0.01 mol) and benzaldehyde (0.01 mol) in absolute ethanol (25 ml) was added piperidine (5 ml), and the mixture was refluxed for 3 h. After cooling, the crystals were filtered off and recrystallised to give *2,3-dihydro-3-piperidinocarbonyl-2-phenylbenzo*[b]*selenophen* (VIa), m.p. 185° (70%) (from hexane–benzene); $\nu_{C=O}$ (KBr) 1 620 cm^{-1}; δ ($CDCl_3$) 1.28 (m) and 3.19 (m, $[CH_2]_5$), 4.25 and 5.25 (ABq, *J* 8 Hz), and 7.15 (m, aromatic) (Found: C, 64.8; H, 5.7; N, 3.7. $C_{20}H_{21}NOSe$ requires C, 64.85; H, 5.7; N, 3.8%). Similar condensation of (I) with benzaldehyde in triethylamine–ethanol gave the corresponding *ester* (VIb), isolated and purified by t.l.c. on silica gel (eluant benzene), $\nu_{C=O}$ (film) 1 750 cm^{-1}, δ [$CDCl_3$; $(Me_3Si)_2O$] 1.09 (t, CH_3), 4.07 (q, CH_2), 4.48 (d)—5.51 (d) (H-2 and -3, *J* 9.3 Hz), and 6.70—7.60 (m, aromatic) (Found: C, 61.7; H, 4.9. $C_{17}H_{16}O_2Se$ requires C, 61.65; H, 4.85%).

[1]*Benzoselenopheno*[3,2-*c*][1]*benzopyran*-1-*one* (XI).—(*a*) A solution of the selenolactone (I) (2 g, 0.01 mol), salicylaldehyde (1.3 g, 0.01 mol), and triethylamine (1 ml) in absolute ethanol (25 ml) was refluxed for 4 h. After cooling, the *product* was filtered off and recrystallised (2.1 g, 70%); m.p. 219° (from toluene) (Found: C, 60.1; H, 2.7. $C_{15}H_8O_2Se$ requires C, 60.2; H, 2.7%).

(*b*) A solution of 2-(methylseleno)phenylacetic acid (11.5 g, 0.05 mol) and salicylaldehyde (6.1 g, 0.05 mol) in acetic anhydride (50 ml) was refluxed for 4 h. The usual purification gave 3-(*2-methylselenophenyl*)*coumarin* (Xb) (10 g, 65%), m.p. 139 (from benzene–hexane); $\nu_{C=O}$ (KBr) 1 700 cm^{-1}; δ ($CDCl_3$) 7.20—7.65 (aromatic) and 2.10 [SeMe, $J(^{77}Se,CH_3)$ 10 Hz] (Found: C, 60.9; H, 3.9. $C_{16}H_{12}O_2Se$ requires C, 60.95; H, 3.85%). A solution of compound (Xb) (0.25 g, 0.000 7 mol) and bromine (0.001 mol) in chloroform (5 ml) was kept for 2 h at room temperature. Use of the bromine–pyridine method,[17] followed by chromatography on silica gel, gave compound (XI) (32%).

3-*Dimethylaminomethylenebenzo*[b]*selenophen*-2(3H)-*one* (VII).—To a solution of the selenolactone (I) (2 g, 0.01 mol) in dimethylformamide (75 ml) was added phosphoryl chloride (2 ml) in the cold. After 2 h at room temperature, the mixture was worked up in the usual manner and the *product* (VII) purified (2.3 g, 90%), m.p. 132° (from hexane); $\nu_{C=O}$ (KBr) 1 640 cm^{-1}; δ ($CDCl_3$) 7.2—7.5 (5 H, aromatic) and 3.3 (s, NMe_2) (Found: C, 52.3; H, 4.3; N, 5.5. $C_{11}H_{11}NOSe$ requires C, 52.4; H, 4.35; N, 5.55%).

The *benzo*[b]*thiophen* analogue of (VII) was obtained in a similar manner in 90% yield; m.p. 115° (from hexane), $\nu_{C=O}$ 1 650 cm^{-1}, δ($CDCl_3$) 7.0—7.2 (5 H, aromatic) and 3.2 (s, NMe_2) (Found: C, 63.9; H, 5.4; N, 6.7. $C_{11}H_{11}NOS$ requires C, 64.4; H, 5.35; N, 6.85%).

Compound (VII) was also obtained, in 75% yield, by condensing compound (I) (0.01 mol) and dimethylformamide dimethyl acetal (0.3 ml) at room temperature in dry benzene (10 ml).

Acetylation of the Selenolactone (I).—(*a*) To a solution of compound (I) (2 g, 0.01 mol) in acetic anhydride (50 ml) was added dropwise boron trifluoride–ether (6 ml) at 0 °C. After 3 h at 100 °C, purification was carried out in the usual manner. The boron complex isolated (m.p. 173°) was hydrolysed with hot 6N-hydrochloric acid giving 3-*acetylbenzo*[b]*selenophen*-2-*ol* (VIIIa), m.p. 93° (from hexane); $\nu_{C=O}$ (KBr) 1 595 cm^{-1}; δ ($CDCl_3$) 2.40 (CH_3), 7.00—7.55 (4 H, aromatic), and 14.52 (OH) (Found: C, 49.8; H, 3.5. $C_{10}H_8O_2Se$ requires C, 50.2; H, 3.35%). The *benzothiophen analogue* of (VIIIa) was obtained in a similar manner (75%), m.p. 105° (from hexane); $\nu_{C=O}$ 1 620 cm^{-1};

δ ($CDCl_3$) 2.46 (CH_3), 7.00—7.5 (4 H, aromatic), and 14.51 (OH) (Found: C, 62.3; H, 4.2. $C_{10}H_8O_2S$ requires C, 62.5; H, 4.15%).

(*b*) A solution of compound (I) (2 g, 0.01 mol) and sodium acetate (4.5 g) in acetic acid (30 ml) and acetic anhydride (50 ml) was refluxed for 16 h. After evaporation, the mixture was taken up in water and the product 2-*acetoxy*-3-*acetylbenzo*[b]*selenophen* (VIIIb) isolated in the usual manner (2.85 g, 91%), m.p. 109° (from hexane); $\nu_{C=O}$ (KBr) 1 655 (ketone) and 1 775 cm^{-1} (phenolic acetate); δ ($CDCl_3$) 2.30 (s) and 2.43 (s) (2 Me) and 6.80—7.40 (4 H, aromatic) (Found: C, 51.2; H, 3.6. $C_{12}H_{10}O_3Se$ requires C, 51.25; H, 3.55%). A similar procedure with the benzothiophen analogue of (I) (3 g, 0.02 mol) gave a mixture of benzothiophen analogues of (VIIIa) and (VIIIb), which were separated by dissolution of (VIIIa) in aqueous sodium hydrogen carbonate. The analogue of (VIIIb) was recrystallised from hexane (1.92 g, 50%); m.p. 87°, $\nu_{C=O}$ 1 650 and 1 770 cm^{-1} (Found: C, 61.6; H, 4.3. $C_{12}H_{10}O_3S$ requires C, 61.5; H, 4.3%). The n.m.r. spectrum showed four signals corresponding to two methyl groups (integration). A similar phenomenon appears in the n.m.r. spectrum of 2-acetoxy-3-acetylindene.[24] By acidification of the hydrogen carbonate solution, the analogue of (VIIIa) was obtained (0.95 g, 20%).

Phosphinic Acids.—*Benzo*[b]*selenophen*-2-*ylphosphinic acid* (XII) was obtained after refluxing for 100 h the selenolactone (I) (0.5 g, 0.000 25 mol) in ethanol (10 ml) and aqueous 50% phosphinic acid (5 ml). It was isolated by acidification of the hydrogen carbonate phase after the usual extraction operations; m.p. 136—138° (from water–ethanol), δ ($CDCl_3$) 6.9—7.9 (4 H, m, aromatic), 7.0 (s, OH, disappearing upon deuteriation), 7.69 (d, PH, $^1J_{PH}$ 597 Hz), and 8.03 (d, H-3, $^3J_{PH}$ 12 Hz) (Found: C, 39.1; H, 2.8. $C_8H_7O_2PSe$ requires C, 39.12; H, 2.85%).

Benzo[b]*selenophen*-3-*ylphosphinic acid*, obtained in the same way from benzo[*b*]selenophen-3(2*H*)-one, melted at 107—108° (from water–ethanol), δ ($CDCl_3$) 7.1—8.2 (5 H, m, aromatic + OH, 4 H after deuteriation), 7.62 (d, PH, $^1J_{PH}$ 579 Hz), and 8.72 (d, H-2, $^3J_{PH}$ 12 Hz) (Found: C, 39.6; H, 2.9. $C_8H_7O_2PSe$ requires C, 39.2; H, 2.85%).

Benzo[*b*]thiophen-3-ylphosphinic acid, obtained from benzo[*b*]thiophen-3(2*H*)-one melted at 87—89° (from hexane–benzene); δ ($CDCl_3$) 7—8.2 (4 H, m, aromatic), 7.64 (d, PH, $^1J_{PH}$ 581 Hz), 8.02 (d, H-2, $^3J_{PH}$ 10 Hz), and 9.4 (s, OH).

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